

OUTGASSING MEASUREMENTS ON MATERIALS IN VACUUM
USING A VACUUM BALANCE AND QUARTZ CRYSTAL BALANCES

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ABSTRACT

For the prediction of cleanliness levels around spacecraft and on critical spacecraft surfaces, one needs - apart from a mathematical model - a number of outgassing characteristics of spacecraft materials. What is required are the time and temperature dependent data such as total outgassing rates, condensation rates of contaminants produced onto surfaces and re-evaporation rates.

As the Micro-VCM outgassing data are of limited value in the prediction of spacecraft contamination, ESTEC developed two outgassing systems using vacuum and quartz crystal balances. The idea behind this development was the desire to obtain Arrhenius-type outgassing equations in which the outgassing is a function of temperature, activation energy and time.

This paper describes the two outgassing systems developed at ESTEC together with some of the results that have been obtained. Also described is a theoretical approach to spacecraft contamination.

1. INTRODUCTION

As spacecraft become more sophisticated and the duration of missions is extended, the need for more stringent control of spacecraft cleanliness is becoming more and more apparent. For experiments which are contamination-sensitive, one requires a prediction of contaminant levels (ref. 1 - 7). However, to predict these levels, one needs not only a mathematical model, but also realistic input data of the outgassing of materials and the condensation and re-evaporation of spacecraft contaminants. It is due to a lack of proper measuring equipment that, so far, not much information in this respect is available.

Lately, however, the situation has changed and significant progress has been made owing to the introduction of quartz crystal microbalances (QCM's) which enable measurement of condensation and re-evaporation of contaminants down to cryogenic temperatures (ref. 8 - 12). Earlier outgassing measurements were based on pressure measurements (ref. 13) and vacuum balance measurements (ref. 14). Mass spectrometers were never widely employed for quantitative outgassing measurements of polymers because of the complexity of outgassing products and calibration problems. In view of the lack of realistic outgassing data, information obtained by application of the well-known Micro-VCM method has been used for a theoretical approach to the Kinetics of outgassing (ref. 15).

An attempt has been made to also calculate theoretical outgassing figures on the basis of the Langmuir evaporation theory (ref. 16 & 17), but the results obtained are of rather limited value since they are only valid for pure materials such as oils, greases, etc.

Considering that the outgassing products of polymers consist, in general, of limited quantities of many different components and that outgassing and contamination are controlled by some 10 different parameters, it is quite obvious that a theoretical prediction of outgassing and contamination by polymers is almost impossible (ref. 18). On these grounds, it will be clear that the most one can do is to perform practical tests; to define the limitations on the basis of the results; to find out whether or not a specific theory fits the results and - if possible - how the test can be improved. Naturally, it would be ideal if we could achieve some form of standard test method for the measuring of outgassing, condensation and re-evaporation rates.

2. TEST SYSTEMS

The equipment constructed to perform the outgassing measurements incorporates the advantages offered by combining QCM's with a conventional vacuum balance.

A. Vacuum Balance - Quartz Crystal System I (VBQC-I)

This system (see Fig. 1) consists of a Sartorius 4201 vacuum balance which is provided with a magnetically suspended sample hanger. The balance has a sensitivity of 1×10^{-5} grammes, but due to vibrations as well as temperature and humidity variations in the TQC laboratory, the accuracy is limited to 10^{-4} grammes. The maximum load of the balance is 25 grammes and sample temperature is controlled by an oven around the sample.

The system contains three Celesco 700A quartz crystal microbalances (QCM's) which can measure the amount of material condensed on the exposed crystal down to a few times 10^{-8} g.cm⁻² (sensitivity: 8.9×10^{-9} g.cm⁻² per mV output). The three QCM's can be cooled down to liquid nitrogen temperatures and are generally controlled at -75, -25 and +25°C respectively.

The removable condenser plate with holes in front of the QCM's is also controlled at -75°C as lowest QCM temperature and has a diameter of 146 mm (E 177 cm² area).

The pumping system is a Varian VT-102 ion pumping system, equipped with a Varian-250 quadrupole mass spectrometer permitting analysis of outgassing products which do not condense on the condenser plate, i.e. mainly water, solvents and atmospheric gases. Also forming part of the system are metal gaskets and pressures down to a few times 10^{-9} torr can be obtained.

B. Vacuum Balance - Quartz Crystal System II (VBQC-II)

The second system (see Fig. 2) consists of a Sartorius 4433 vacuum balance which is mounted completely inside the system. Its sensitivity is 1×10^{-7} grammes and the maximum sample load is 3 grammes. Basically, this system is identical to the VBQC-I. The condenser plate has a diameter of 200 mm (E 314 cm² area).

The mass spectrometer is capable of analyzing all outgassing products from the sample through a hole in the condenser plate.

FIG.1 VBQC -I OUTGASSING SYSTEM

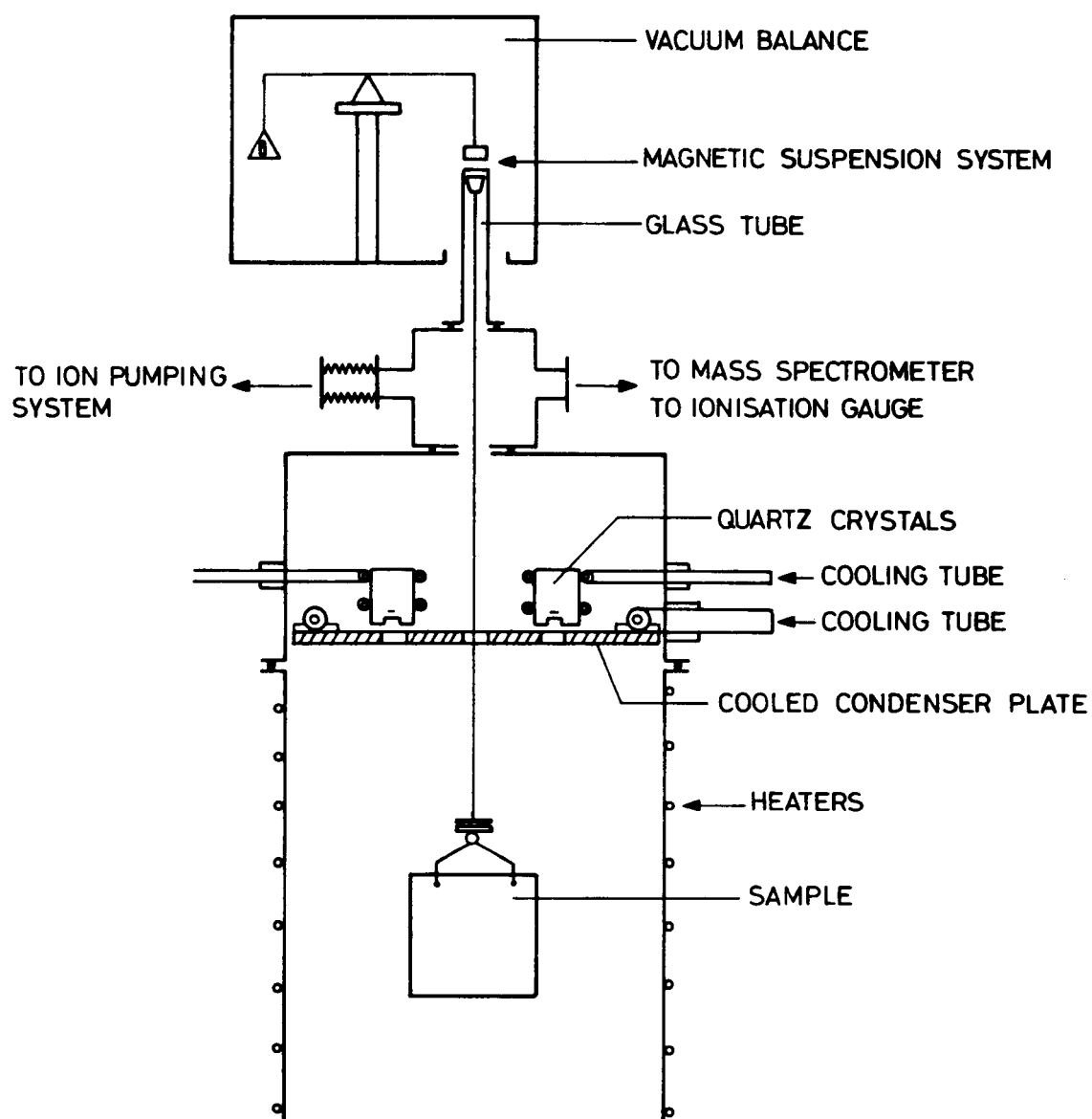
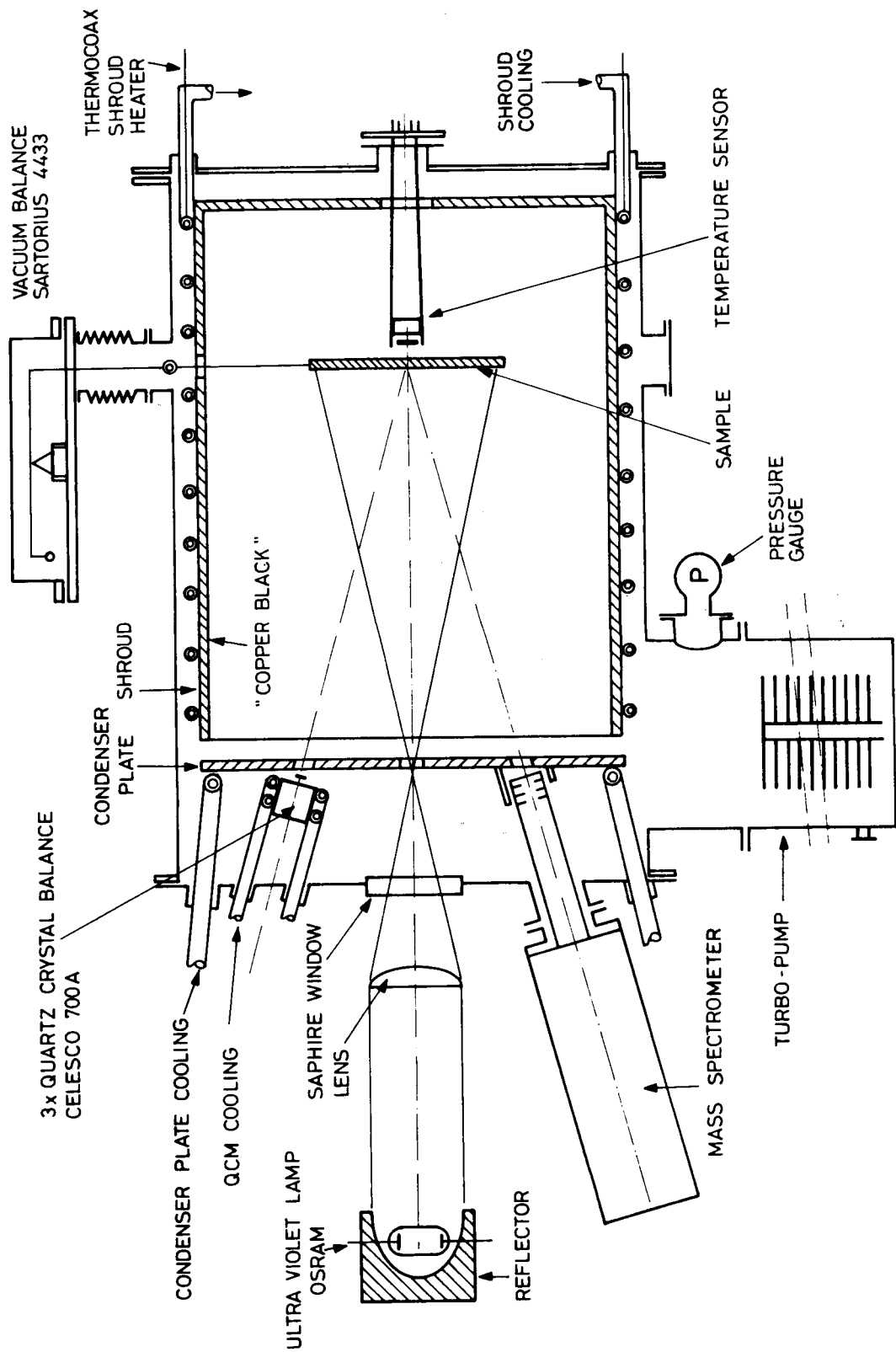


FIG 2 VBQC-II OUTGASSING SYSTEM



An additional feature is the sapphire window through which the sample can be irradiated by ultra-violet light. The sample can be heated either by radiation from the outside through this window or by radiation from the surrounding shroud.

The latter can be cooled down to liquid nitrogen temperature or heated to around 300°C.

The system is furthermore equipped with a Balzers turbopump and metal gaskets. The ultimate pressure is in the order of a few times 10^{-9} torr.

3. OUTGASSING MEASUREMENTS ON SPACELAB THERMAL BLANKET

A. Test Method

Three vacuum balance tests (VBQC tests), using the VBQC-I system described under 2A, were performed on the same thermal blanket sample at temperatures of respectively 80, 80 and 125°C so as to simulate successive SPACELAB flights. Prior to each test, the sample was conditioned at 20°C and 65% relative humidity over a period of at least one week. From the recorded mass versus time curves, the following outgassing data were obtained:

- Total mass loss (% TML). The "buoyancy effect" was assumed to be 20 mg on this sample of 20 grammes.
- Total mass loss rate.

Immediately after the vacuum test, the water vapour regain (% WVR) was measured at 20°C and 65% RH over a period of 24 hours, using a normal balance under atmospheric conditions.

The three quartz crystal balances were controlled at temperatures of respectively -75, -25 and +25°C while the condenser plate was controlled at -75°C.

From the measurements of the frequency of the quartz crystals, the following outgassing data as a function of time were obtained:

- Collected Volatile Condensable Material (% CVCM),
- Outgassing rate of condensable material.

To obtain the total of condensable material, the data from the quartz crystals ($1 \text{ Hz} \approx 4.4 \times 10^{-9} \text{ g.cm}^{-2}$) were multiplied by a factor of 177 (the condenser plate's surface area in cm^2).

B. Material Description

The thermal blanket sample of 6.5 x 30.5 cm (= 198 cm² area) had a mass of 19.9621 grammes ($\approx 101 \text{ mg.cm}^{-2}$). The materials used for this blanket were, according to the manufacturer (Aeritalia):

<u>HPI material</u>	: 19 layers of 0.3 mil Kapton, goldized on both sides (Specification SP-AIT-0035);
<u>Spacing material</u>	: 20 layers of Dacron net. Specification SP-AIT-0033;
<u>Inner protective layers</u>	: Goldized Kapton 0.5 mil reinforced with Nomex net. Specification SP-AI-0030;
<u>Outer protective layers</u>	: Teflon-coated fibreglass cloth (Beta cloth). Specification SP-AI-0038;
<u>Goldized Kapton tape</u>	: Silicone pressure-sensitive adhesive. Specification SP-AI-0034;
<u>Goldized Kapton tape</u>	: Reinforced with glass fibre, pressure-sensitive adhesive;
<u>Vents</u>	: Fibre glass Narmco 506/181;
<u>Thread</u>	: Nomex. Specification MIL-T-43636, Type I, size ff;
<u>Fasteners</u>	: AMOCO Torlon 4203;
<u>Bonding material</u>	: RTV-566 silicone adhesive.

C. Results

The final results of the three successive VBQC tests on the same thermal blanket are listed in Table 1 hereunder.

TABLE 1 - VBQC OUTGASSING DATA OF SPACELAB THERMAL BLANKET

Test	% TML	% CVCM -75°C	% CVCM -25°C	% CVCM +25°C
VBQC-021 at 80°C/170 h.	0.804	0.0133 ⁽¹⁾	0.0080	≤ 0.0003
VBQC-022 at 80°C/107 h.	0.900	0.0015	0.0006	≤ 0.0001
VBQC-24 at 125°C/165 h.	0.822	0.0104 ⁽²⁾	0.0077	0.0004

Notes

(1) The recuperated contaminants from the condenser plate, after

the VBQC-21 test, amounted to 2.98 mg which corresponds to a percentage of 0.0149%. This is in good agreement with the value obtained from the quartz crystal balance at -75° C. The infra-red spectrum of the recuperated contaminants indicated hydrocarbons, phthalate esters and methyl silicones.

- (2) The recuperated contaminants from the condenser plate, after the VBQC-024 test, amounted to only 1.1 mg (\pm 0.0055%). This lower value can be partly attributed to a condense cooling failure at the end of the test, resulting in a partial re-evaporation of the collected contaminants. The infra-red spectrum of the "stripped" screen contaminants indicated many more silicones than the spectrum of test VBQC-021.

The water vapour regain (WVR) by the thermal blanket after exposure to 65% RH at 20° C after 24 hours is listed in Table 2 hereunder.

TABLE 2 - WATER VAPOUR REGAIN OF THERMAL BLANKET

Test	%WVR
VBQC - 021	0.88
VBQC - 022	0.73
VBQC - 024	0.67
Average	0.76

The outgassing rates derived from the thermal blanket during the three VBQC tests are given in Figures 3, 4 and 5*.

* Conversion from $\%.S^{-1}$ to $g.cm^{-2}.S^{-1}$, multiply by 1×10^{-3} .

Conversion from $\%.S^{-1}$ to $torr.l.cm^{-2}.S^{-1}$, multiply by 0.95 (M = 18).

D. Conclusions drawn from Thermal Blanket Outgassing Tests

- The total mass loss after 7 days is 0.85% (average value), i.e. approximately the same percentage as the water vapour regain after the tests (0.76%).

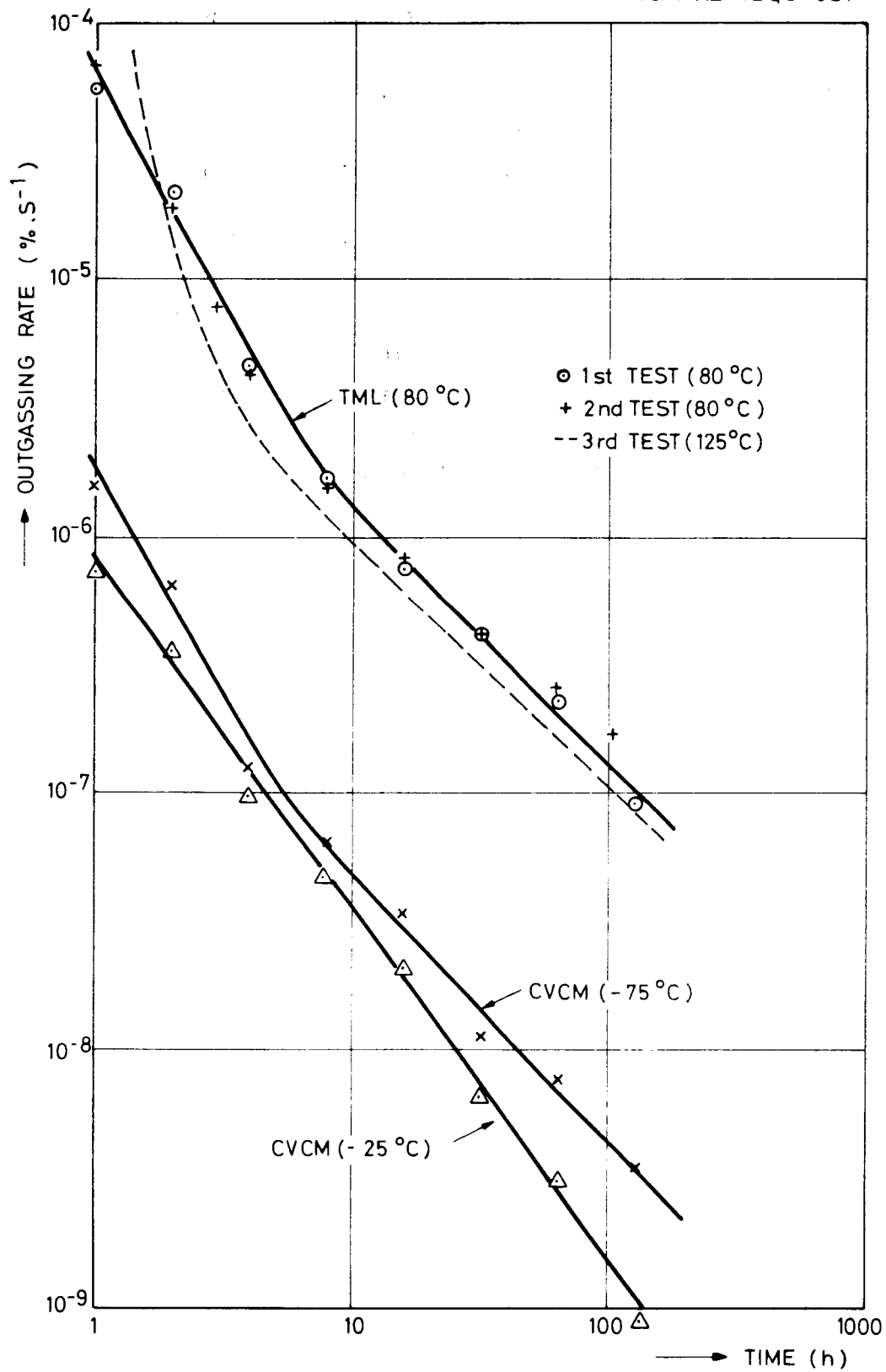


FIG.3 OUTGASSING RATE OF SPACELAB THERMAL BLANKET
(mass = 20 g , area 200 cm²)

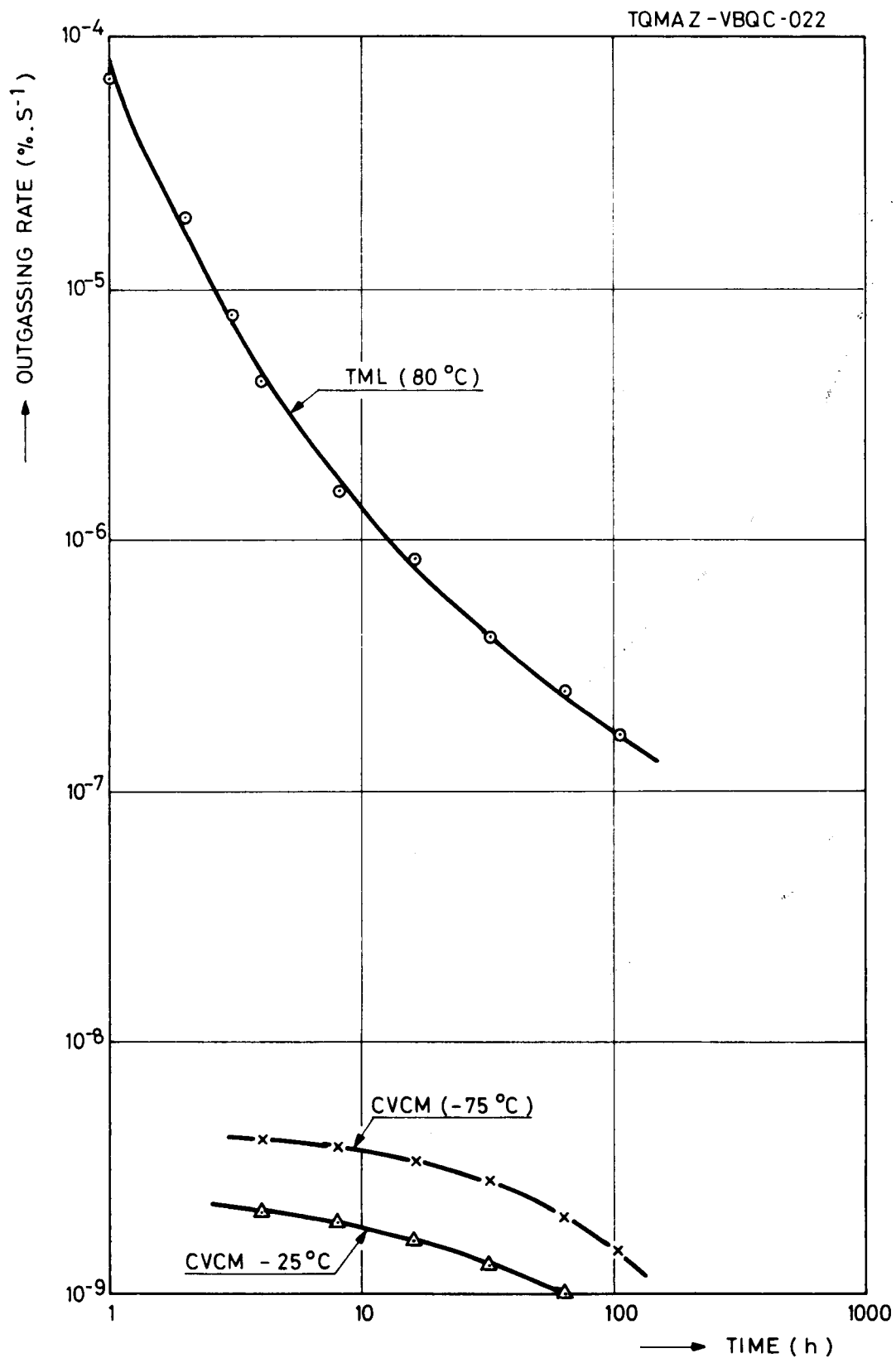


FIG.4 OUTGASSING RATE OF SPACELAB THERMAL BLANKET (2nd TEST)

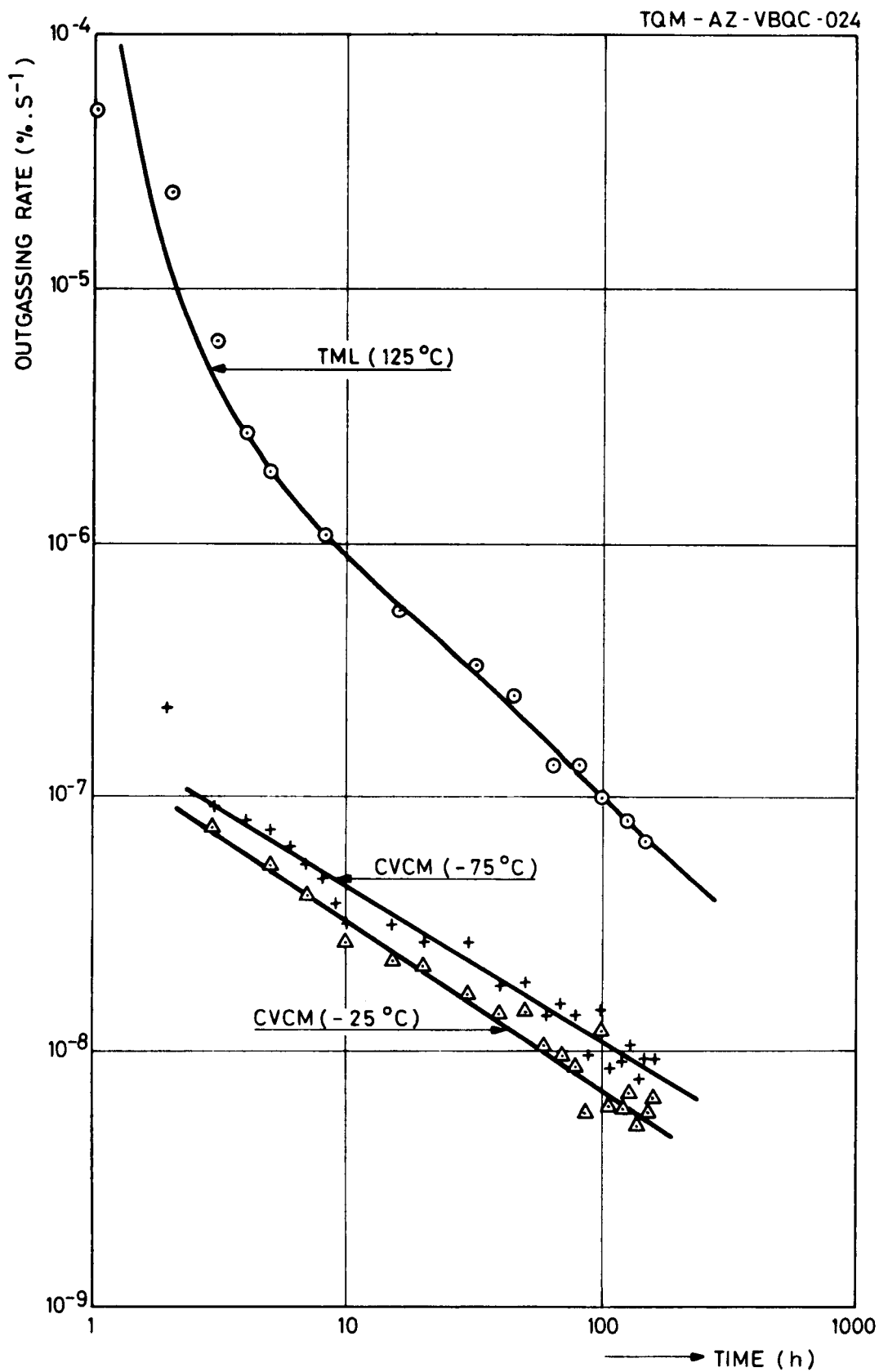


FIG.5 OUTGASSING RATE OF SPACELAB THERMAL BLANKET (3rd TEST)

- The total outgassing rate is almost independent of the temperature. This corresponds to a low "desorption"-activation energy.
 - The amount of condensable material collected during the second test at 80° C was only 10% of the amount collected during the first test. (A vacuum bake proves to be an efficient way of releasing volatile condensable contaminants).
- The CVCM outgassing rate during the second test was roughly the same as that at the end of the first test.
- From the initial outgassing rates of the condensable materials during the third test at 125° C and the final outgassing rates during the second test at 80° C, the activation energies for condensable outgassing can be calculated according to Arrhenius's law:-

$$\frac{V_1}{V_2} = e^{-\left(\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)}$$

TABLE 3 - ACTIVATION ENERGIES OF CONSENSABLE MATERIAL

	V1/80° C	V2/125° C	Activation Energy
CVCM - 75° C	1.5 x 10 ⁻⁹	9.1 x 10 ⁻⁸	25,600 calmol ⁻¹
CVCM - 25° C	8 x 10 ⁻¹⁰	7.2 x 10 ⁻⁸	28,100 calmol ⁻¹

From the fact that the condensable outgassing rates tend to drop below the 10⁻⁸ % .S⁻¹ at the end of the test at 125° C, it may be concluded that the outgassing of the condensable material is unlikely to be caused by thermal degradation because no steady state outgassing level is reached!

4. OTHER OUTGASSING DATA FROM VBQC-I TESTS

The final results of a number of VBQC-I tests are listed in Table 4 hereunder and partly plotted in Figure 6 to give an impression of the effect of temperature on condensable materials.

TABLE 4 - VBQC-I OUTGASSING DATA

Material	Test	Time/Temp.	% TML	% RML	% CVCM -75° C	% CVCM -25° C	% CVCM +25° C
Chemglaze Z 202	001	160h/125°C	2.42	-	0.082	0.033	≤ 0.0002
Araldite AW 106	005	24h/125°C	2.43	-	0.173	0.0565	≤ 0.007
Solithane 113	007	24h/125°C	0.26	-	0.025	0.014	≤ 0.001
Honeycomb OTS	009	36h/100°C	0.293	0.073	0.0026	0.0010	0.0001
Honeycomb + RTV-560	010	18h/100°C	0.370	0.088	0.0250	0.0055	0.0001
Chemglaze II A-276	019	160h/125°C	2.07	1.45	0.232	0.064	0.028
Araldite AV 100	026	112h/125°C	1.70	0.87	0.060	0.045	0.025
Super Koropon *	027	142h/125°C	4.53	3.44	0.134	0.077	-

* After vacuum post cure 320h/80° C.

The curves drawn through the three points in Figure 6 give the impression that the CVCM at intermediate temperatures can be found easily. However, a theoretical contamination curve for ethylhexylphthalate indicates a sudden re-evaporation around 0° C. None of the practical curves is similar to the theoretical curve, which may be explained by the fact that the condensable material consists of several components, e.g. gaschromatograph mass spectrometer analyses of the material condensed at -75° C, originating from a honeycomb panel with RTV-560 adhesive on top, indicated some 20 different components (ref. 19).

5. THEORETICAL CONTAMINATION EQUATIONS

Contamination of a surface by outgassing products, originating from an outgassing source, can be expressed by the following equation:-

$$Q_S = Q_C - Q_L \quad (\% \cdot S^{-1})^* \quad \text{EQUATION 1}$$

where:-

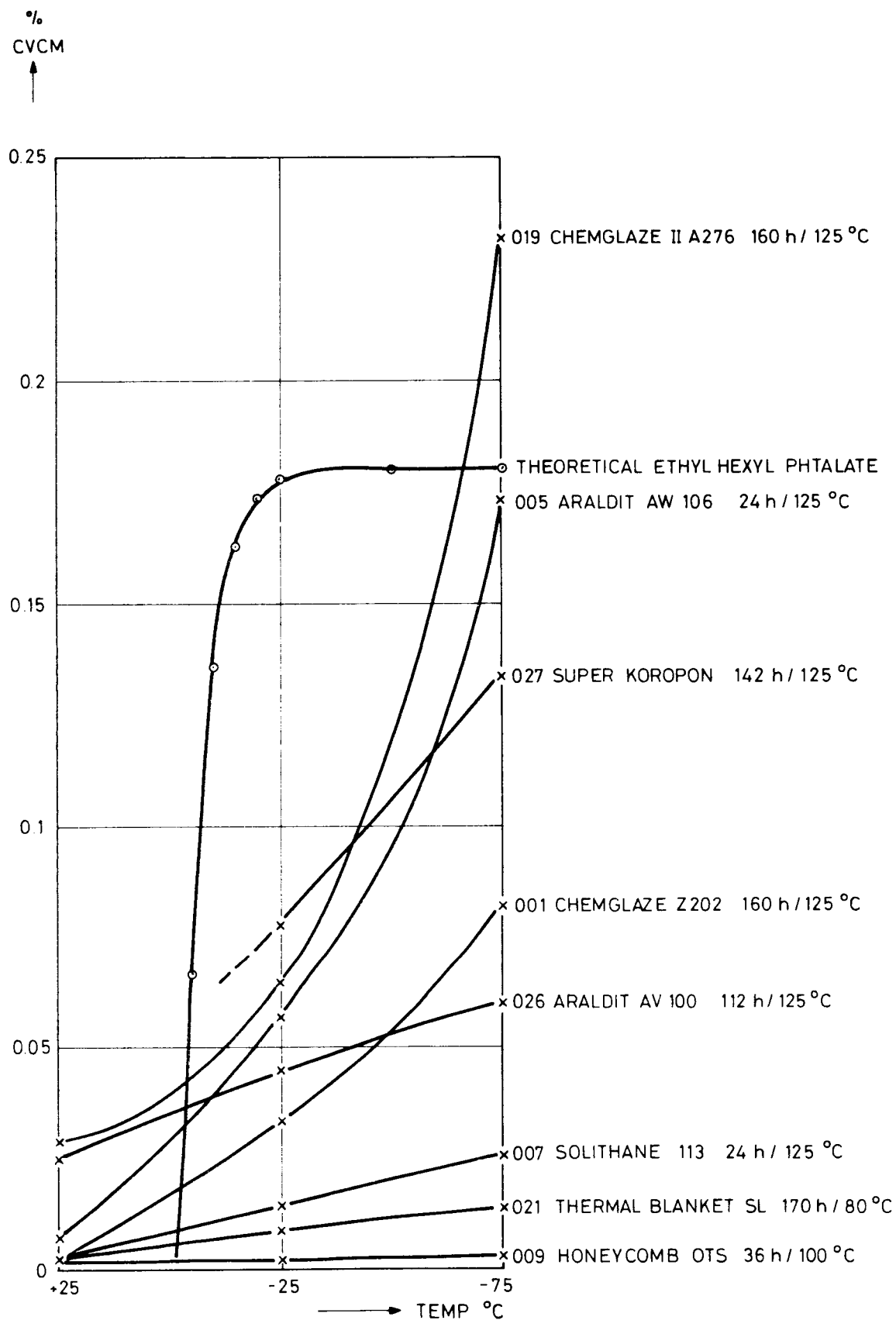


FIG.6 CONDENSIBLE MATERIAL AT DIFFERENT CONDENSER TEMPERATURES
(VBQC - TESTS)

Q_S = mass change of contaminants on a surface or contamination flux,

Q_C = captured flux,

Q_L = leaving flux.

*For simplification purposes, the fluxes are expressed in $\% \cdot S^{-1}$ based on the mass (M) of the outgassing material.

The captured flux can be further expressed by:

$$Q_C = F\sigma Q_O \quad (\% \cdot S^{-1}) \quad \text{EQUATION 2}$$

where:

F = view factor, the fraction of mass leaving the outgassing source which is capable of striking a known surface of area A (cm^2),

σ = capture coefficient, the fraction of mass striking a surface which is not reflected, i.e. is absorbed (other terms used in literature are absorption coefficient, condensation coefficient and accommodation coefficient),

Q_O = outgassing flux of the source ($\% \cdot S^{-1}$).

The leaving flux Q_L can be expressed by the Langmuir equation for evaporation:

$$Q_L = 0.06 P_S \sqrt{\frac{M}{T}} \cdot k \cdot A \cdot \frac{100}{m} \quad (\% \cdot S^{-1}) \quad \text{EQUATION 3}$$

where:

P_S = saturated vapour pressure of contaminants (Torr),

M = molecular mass,

T = temperature (K),

k = evaporation factor; this factor was introduced in view of possible non-evaporation of the first monolayer (s) due to Van de Waals' forces and also in view of possible repolymerization of, or reaction between the captured contaminants,

A = area of contaminated surface (cm^2),

m = mass of outgassing source (g).

Combination of equations 1, 2 and 3 gives:

$$Q_S = F\sigma Q_O - 0.06 P_S \sqrt{\frac{M}{T}} \cdot k \cdot A \cdot \frac{100}{m} \quad (\% \cdot S^{-1}) \quad \text{EQUATION 4}$$

or, simplified:

$$Q_S = F_2 Q_O - Q_L$$

(%.S⁻¹)

EQUATION 5

A. CALCULATION OF EXPECTED SPACECRAFT CONTAMINATION BASED ON MEASURED CONTAMINATION FLUXES

Expected condensable contamination in a given application can be evaluated from equation 6 which is based on an assumed linear relationship between contamination flux (Q_S) and view factor F :

$$Q_{S2} = \frac{F_2}{F_1} Q_{S1}$$

(%.S⁻¹)

EQUATION 6

where:

Q_{S2} = expected contamination flux (%.S⁻¹),

F_2 = realistic view factor,

F_1 = view factor of VBQC test,

Q_{S1} = contamination flux during VBQC test (%.S⁻¹).

B. CALCULATION OF EXPECTED SPACECRAFT CONTAMINATION USING THE STICKING COEFFICIENT

Certain contamination models use the sticking coefficient:

S = fraction of impinging flux (FQ_O), which sticks permanently onto the surface, or

$$S = \frac{Q_S}{FQ_O}$$

EQUATION 7

Expected spacecraft contamination can be calculated using equation 7 for a given application, where:

F_2 = view factor and

Q_{S2} = the expected contamination level.

$$Q_{S2} = S F_2 Q_O$$

(%.S⁻¹)

EQUATION 8

The sticking coefficient has to be measured from tests. The VBQC tests give Q_S and Q_O data, so that - using equation 7, we obtain:

$$S = \frac{Q_{S1}}{F_1 Q_O}$$

EQUATION 9

Combination of equations 8 and 9 gives:

$$Q_{S2} = \frac{F_2}{F_1} \cdot Q_{S1} \quad (\%S^{-1}). \quad \text{EQUATION 10}$$

Via determination of the sticking coefficient using the VBQC test, we arrive at the same equation 6 as in paragraph 5, which is not surprising. The sticking coefficient "S" may be expressed also as the capture coefficient " σ " minus the ratio of leaving flux Q_L to impinging flux FQ_O by the combination of equations 5 and 7:

$$S = \sigma - \frac{Q_L}{FQ_O} \quad \text{EQUATION 11}$$

This equation demonstrates that the sticking coefficient changes with the impinging flux FQ_O because the leaving flux Q_L (i.e. the evaporated flux) is constant for a given temperature of the condenser and " σ " is supposed to vary only slightly with temperature.

The sticking coefficients of the thermal blanket contaminants, calculated on the basis of equation 7, from Q_S and Q_O fluxes which were obtained from VBQC tests (paragraph 3) are certainly not constant, as can be seen from Table 5 hereunder.

TABLE 5 - STICKING COEFFICIENTS OF THERMAL BLANKET CONTAMINANTS

Test	Sticking coefficient at -25°C			Sticking coefficient at -75°C		
	1 hour	10 hours	100 hours	1 hour	10 hours	100 hours
1st at 80°C	1.3×10^{-2}	2.6×10^{-2}	1.2×10^{-2}	2.9×10^{-2}	3.6×10^{-2}	3.2×10^{-2}
2nd at 80°C	3.0×10^{-5}	1.3×10^{-3}	4.7×10^{-3}	5.6×10^{-5}	2.6×10^{-3}	8.8×10^{-3}
3rd at 125°C	1.5×10^{-3}	3.4×10^{-2}	7.0×10^{-2}	1.9×10^{-3}	4.9×10^{-2}	1.1×10^{-1}

The fact that the sticking coefficients shown in Table 5 are not constants can be explained by considering equation 7. As will be seen, "S" is the ratio of Q_S (contamination flux consisting of high molecular weight components: hydrocarbons, esters and silicones) and the impinging flux FQ_O (i.e. mainly water). Thus, the outgassing of completely different components is being compared.

The method used to predict spacecraft contamination by means of equation 8 (the sticking coefficient method) is much more complicated than prediction

according to equation 6 because Q_o and "S" both change with time and the second method does not even consider Q_o . The final results are, however, the same; both methods suffer from the same error of the non-proportional function of Q_L with FQ_o in equation 11.

The prediction of spacecraft contamination according to the two above methods is only absolute if the test conditions are the same as the actual conditions, i.e. if the amount of captured contaminants per unit condenser area is the same. In other words, the same configuration factor "K" must be used in equation. Should the predicted factor "K" be lower than the "K" factor of the VBQC test, then the predicted contamination level may be too high because the ratio $\frac{Q_L}{FQ_o}$ will probably increase (equation 11).

7. IDEAL OUTGASSING MEASUREMENTS

As mentioned in the preceding paragraph, ideal measurements are those that relate to "configuration" type samples. In practice, however, they are difficult to perform by means of vacuum balances due to accuracy and mass limitations. An alternative method consists of performing a standard test and measuring all required parameters. This will enable the prediction of absolute levels instead of pessimistic ones. The parameters required are those mentioned in equation 5, viz.:

$$Q_S = FQ_o - Q_L \quad (\%S^{-1}). \quad \text{EQUATION 12}$$

The contamination flux Q_S and the total outgassing flux Q_o can be measured using the VBQC systems. The view factors are known and the unknown "σ" = capture coefficient and the Q_L = leaving flux according to the Langmuir evaporation equation can be measured by shielding the contaminant sensors (QCM's) from the outgassing source. This means that the view factor "F" becomes zero, so that Q_S becomes Q_L . In practice, this implies that the contaminant level will decrease as a result of re-evaporation of the contaminants on the QCM. Once Q_L is known, "σ" may be calculated from equation 5.

To obtain accurate data, it is important that Q_o does not change too much during the shielding period. This period should be, therefore, as short as possible.

A practical means of measuring Q_L is given in Figure 7.

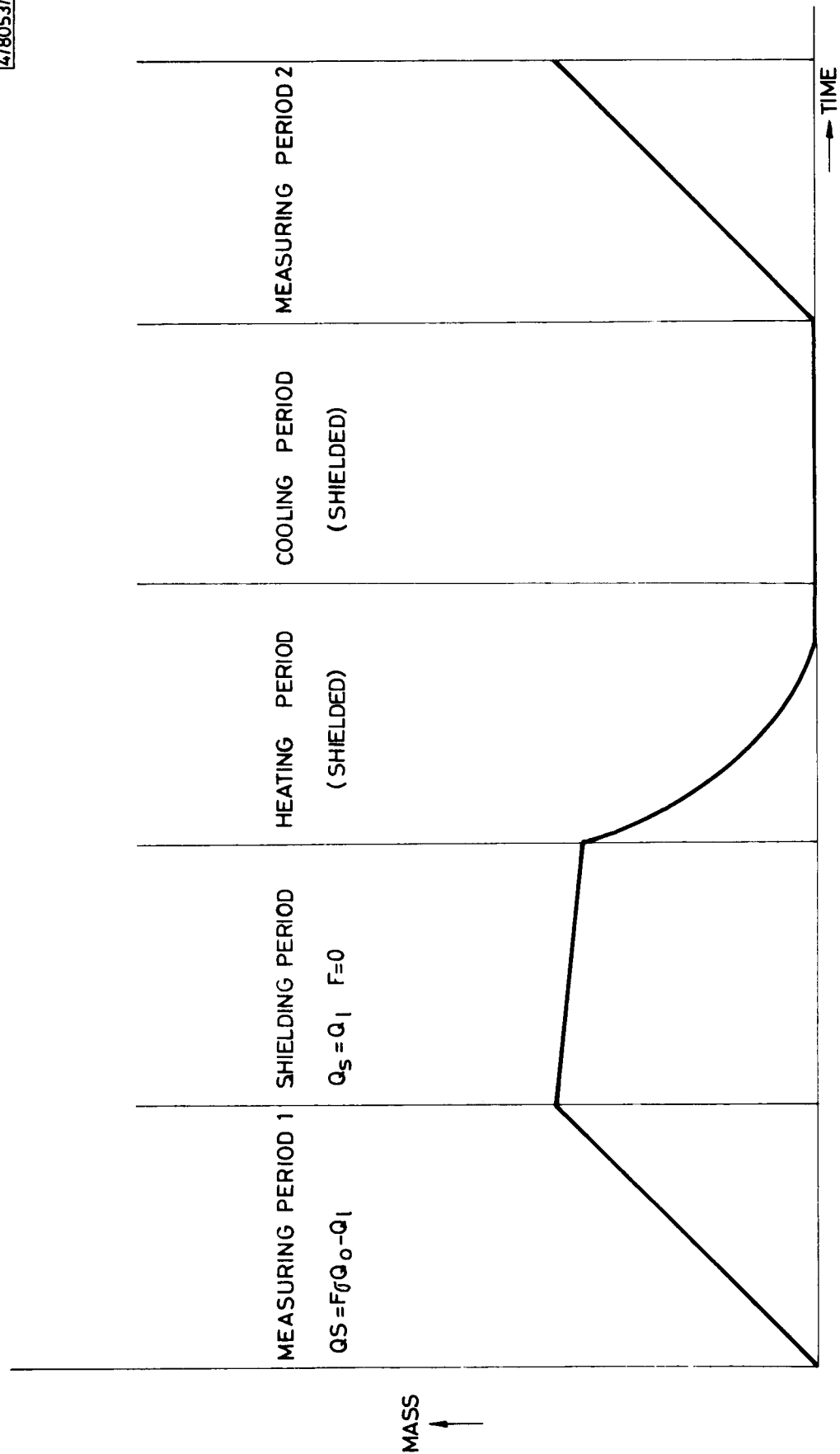


FIG.7 MEASURING OF CONTAMINATION FLUX Q_S LEAVING FLUX Q_I ACCORDING TO $Q_S = F \sigma Q_0 - Q_I$

This type of test can produce curves of Q_S , Q_O , Q_L and " σ " as a function of time and temperature.

8. RE-EVAPORATION OF CONTINUOUSLY COLLECTED CONTAMINANTS AT THE END OF A TEST

The standard VBQC test method involves the collection of all contaminants on the QCM's during the test and their subsequent re-evaporation at the end of the test by heating the QCM's. This method of continuous collection may result in incorrect contamination fluxes (Q_S), especially when these fluxes drop by some order of magnitude during a test. An example, based on the Q_S curve (CVCM - 75°C) in Figure 3 shows how it is possible to obtain such incorrect contamination fluxes:

The initially measured contamination flux of $2 \times 10^{-6} \text{ \%} \cdot \text{S}^{-1}$ is supposed to have a leaving flux Q_L of $1 \times 10^{-8} \text{ \%} \cdot \text{S}^{-1}$.

After 100 hours, the measured flux dropped to $4 \times 10^{-9} \text{ \%} \cdot \text{S}^{-1}$. Supposing that the leaving flux at that time is still the same as during the initial period, i.e. $1 \times 10^{-8} \text{ \%} \cdot \text{S}^{-1}$, then the real contamination flux, after 100 hours, should be $1.4 \times 10^{-8} \text{ \%} \cdot \text{S}^{-1}$ instead of the measured $4 \times 10^{-9} \text{ \%} \cdot \text{S}^{-1}$.

The theoretical error is not verified in this case because the initial contamination flux Q_S , measured with a clean QCM during the second test on the thermal blanket, is close to the final Q_S during the first test, respectively $4 \times 10^{-9} \text{ \%} \cdot \text{S}^{-1}$ and $3 \times 10^{-9} \text{ \%} \cdot \text{S}^{-1}$ (see Figures 3 and 4).

Re-evaporation of contaminants at the end of a test by heating the QCM's results in re-evaporation rates as a function of time and temperature. Derived from these re-evaporation rates can be the effective vapour pressure

$$P_S^1 = P_S \sqrt{\frac{M}{T}} \cdot k. \quad (\text{torr}) \text{ at different temperatures. (See equation 12).}$$

From the above measurements, the relation between effective vapour pressures and composition of the collected contaminants may be calculated (see Figure 8). Conversion of these effective vapour pressures, obtained at different temperatures, to effective vapour pressures at any temperature is possible by interpolation and extrapolation as shown in Figure 11.

From the curve of effective vapour pressure versus composition of collected contaminants at constant temperature (similar in appearance to Figure 9), the amount of contaminants which will re-evaporate in the predicted model can be

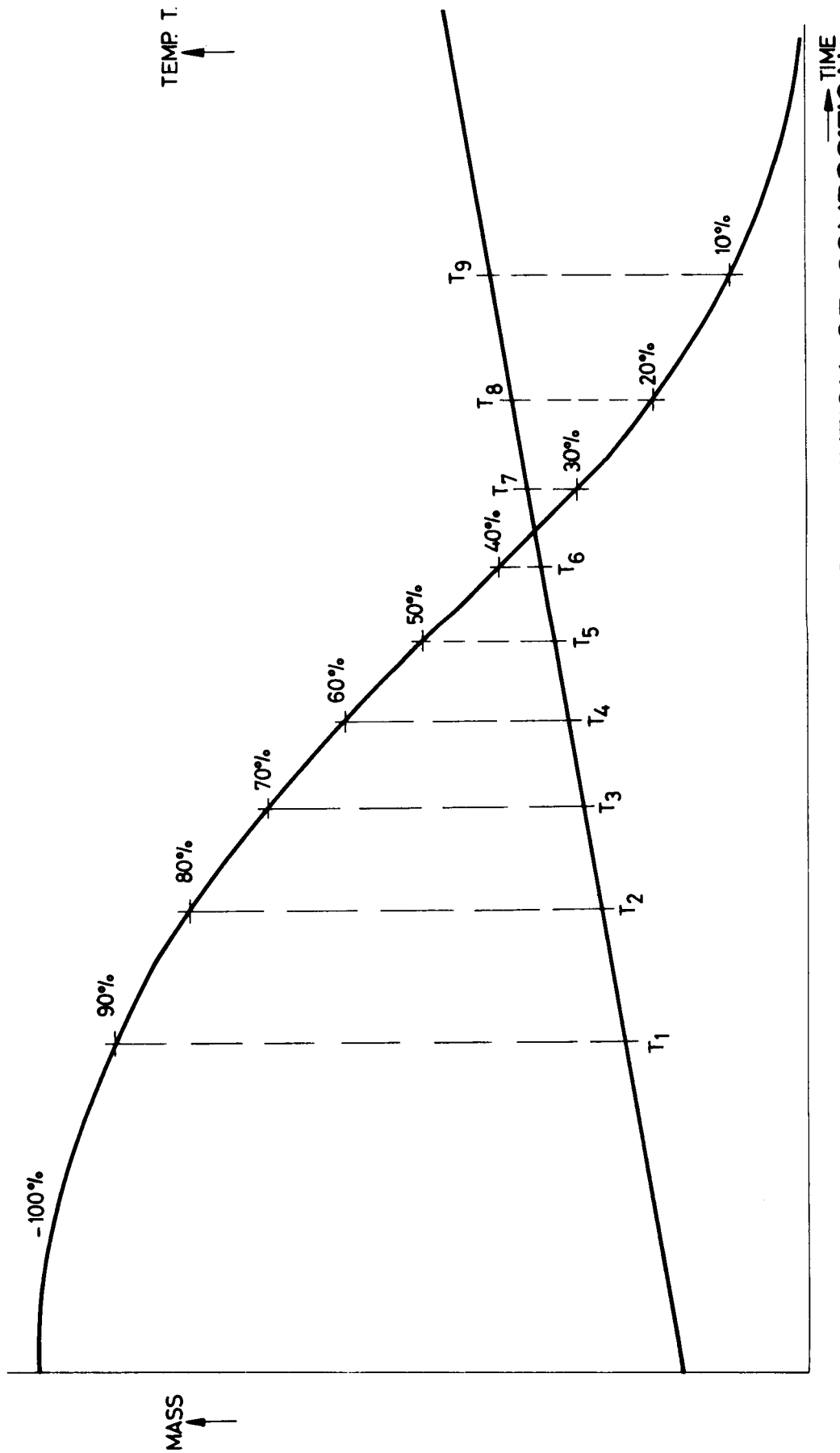


FIG.8 DETERMINATION OF VAPOUR PRESSURE AS A FUNTION OF COMPOSITION FROM RE-EVAPORATION RATES OF CONDENSED CONTAMINANTS

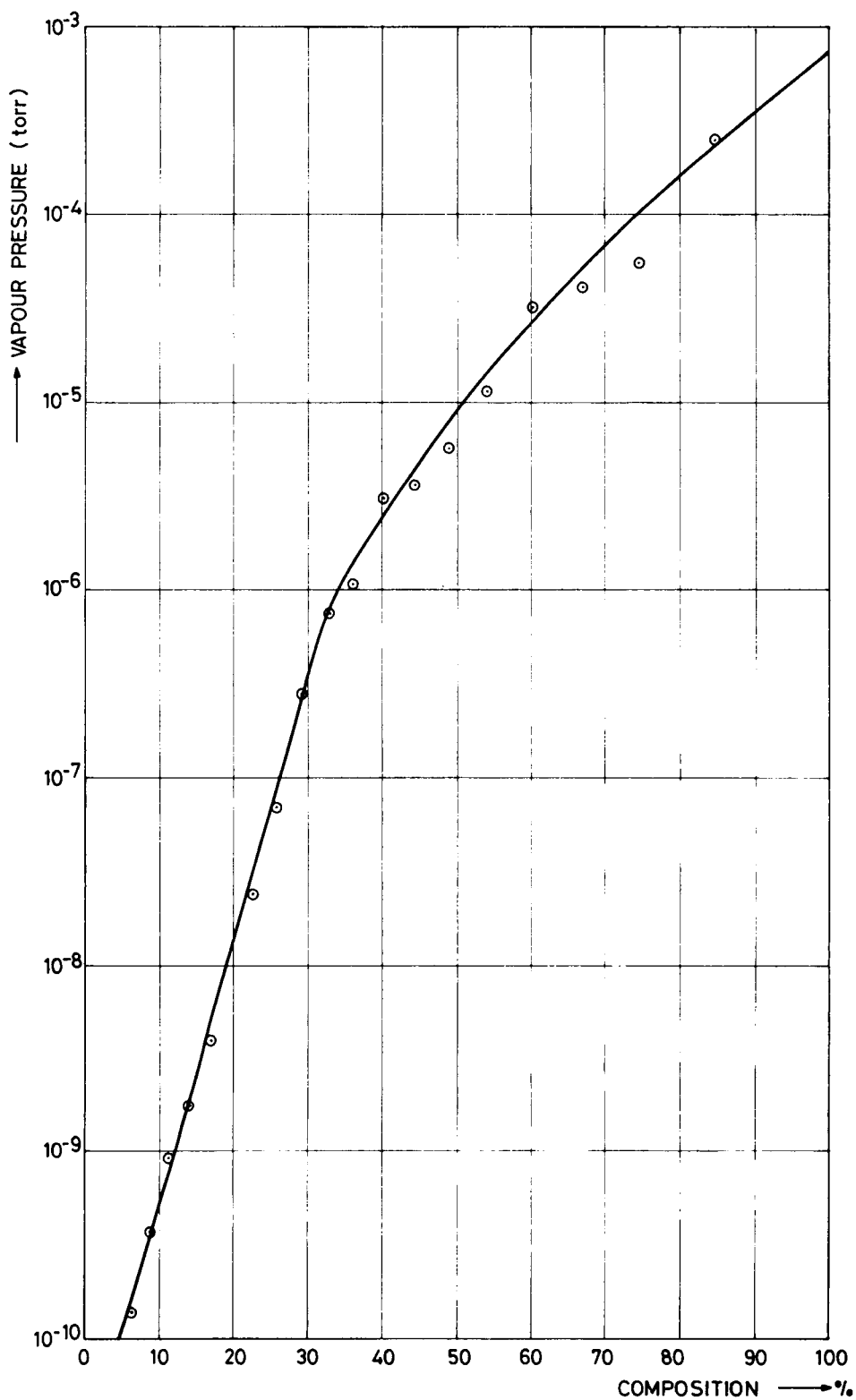


FIG.9 VAPOUR PRESSURE AT 25 °C OF MATERIAL CONDENSED AT -75 °C ORIGINATING FROM ARAIDIT AW 106 AS A FUNCTION OF COMPOSITION (REF. VBQC -005)

calculated, but only in the case where the "configuration" factor "K" is smaller than the "K" factor during the test. The latter operation is a re-evaporation correction of the pessimistic prediction mentioned in the last alinea of paragraph 6.

Again, there is an uncertainty because the above corrections are based on a constant composition of the collected contaminants. It could be imagined that - to the contrary - the average vapour pressure of the contaminants will decrease with time and that, thus, the composition will change.

9. VAPOUR PRESSURES AND COMPOSITION OF CONTAMINANTS (calculated from contamination flux (Q_S) measurements at different temperatures)

A third method of obtaining the effective vapour pressure and composition of contamination flux Q_S is based on the three different Q_S values obtained with the QCM's at different temperatures. The advantage of this method over the one described in paragraph 8 is that this method can be applied at any time during the test. In this method, the flux Q_{S1} at temperature T_1 is compared to flux Q_{S2} at $T + \Delta T$ and it is assumed that the difference between these two fluxes is caused by the re-evaporation of the contaminants. This can be expressed as follows:

$$Q_{S1} = \sigma_1 F Q_O - 0.06 P_{S1} \sqrt{\frac{M}{T}} \text{ k.a. } \frac{100}{m} \quad (\text{from equation 4})$$

$$Q_{S2} = \sigma_2 F Q_O - 0.06 P_{S2} \sqrt{\frac{M}{T}} \text{ k.a. } \frac{100}{m} \quad (\text{from equation 4})$$

$$\Delta Q_S = \sigma F Q_O - P_S \times C$$

EQUATION 13

or

$$\Delta P_S = \frac{\Delta Q_S}{\frac{\Delta \sigma F Q_O}{\Delta P_S} - C}$$

EQUATION 14

In equation 14, it can be assumed that $\Delta \sigma$ is negligible compared to ΔP_S because σ is expected to vary little with temperature and P_S varies some 20% per degree! The further calculation of effective vapour pressures and composition of contaminants is similar to that mentioned in paragraph 8. The results of this approach on an Araldite AW 106 outgassing test are shown in Figure 9.

One of the problems of determination of vapour pressures of condensable contaminants as a function of temperature by measuring the re-evaporation rates from the QCM's is the accuracy of the temperature measurement of the QCM. Our present QCM's - in principle two quartz crystals between which a platinum resistor measures the average temperature of the two crystals; one crystal is shielded and the other exposed to the outgassing flux to be measured - indicated an error in temperature measurement of $\sim 20^\circ\text{C}$ during a thermal cycling test of a solar array. The QCM temperature reading during that test was -150°C , the exposed crystal facing the solar array at $+55^\circ\text{C}$ indicated at that moment a water re-evaporation rate which corresponded to a temperature of -130°C (reference 22).

10. IDEAL CASE OF NO SURFACE CONTAMINATION

Theoretically, one can avoid surface contamination as can be seen from equation 4 hereunder:

$$Q_S = F Q_O - 0.06 P_S \frac{M}{T} \cdot k.A. \frac{100}{m} \quad (\text{EQUATION 4})$$

No surface contamination means $Q_S = 0$ or in formulation:

$$F Q_O = 0.06 P_S \frac{M}{T} k.A. \frac{100}{m} \quad (\% \cdot \text{s}^{-1}) \quad (\text{EQUATION 15})$$

Introduction of the configuration factor "K" which can be expressed as:

$$K = \frac{F \cdot m}{6A} \quad (\text{EQUATION 16})$$

and combination of equations 12, 15 and 16 gives the relation between the effective vapour pressure P_S^1 and the total outgassing flux:

$$P_S^1 = K Q_O \text{ (torr)}. \quad (\text{EQUATION 17})$$

This means that a contaminating component of which the outgassing flux is Q_O and the effective vapour pressure above the one calculated from equation 16 will not contaminate a surface under the conditions fixed by "configuration" factor "K."

In most cases, it will be difficult to realize no surface contamination, but in practice one can go at least some way towards achieving this goal by:

- 1) reduction of view factor "F" by shielding the critical surface;
- 2) reduction of capture coefficient "σ" (main problem is how?);
- 3) reduction of Q_O . In practice, this means the Q_S at the temperature of the critical element by:

- (a) selection of proper materials,
 - (b) reduction in temperature of outgassing source,
 - (c) application of a shutter, so that the critical surface does not see the outgassing source until after a certain time when the outgassing has dropped below a certain level;
 - (d) covering the outgassing source by a low outgassing material of low permeability;
 - (e) pre-degassing of materials;
- 4) application of the lowest material mass possible;
 - 5) augmentation of vapour pressure by increasing the critical surface temperature.

If the above actions cannot prevent surface contamination, then a periodical de-contamination of the critical surface is possible, e.g. by heating. The configuration factor "K" for the three outgassing systems at ESTEC has been calculated from equations 15 and 16 assuming that the capture coefficient = 1. The relevant data are given in Table 6 and the function of "K" with vapour pressure and outgassing flux is plotted in Figure 10.

TABLE 6 - CONFIGURATION FACTOR "K" FOR OUTGASSING SYSTEMS

System	m g	A cm ²	K
Micro-VCM	0.2	7	5×10^{-3}
VBQC-I	20	176	2×10^{-2}
VBQC-II	1	314	5×10^{-4}

An outgassing flux of $1 \times 10^{-6} \text{ g.s}^{-1}$ corresponding to 0.1% CVCM according to the micro-VCM test during 24 hours will just re-evaporate if the vapour pressure of the material is 5×10^{-9} torr. This vapour pressure at 25°C corresponds to the vapour pressure of triacontaan $\text{C}_{30}\text{H}_{62}$ (see Figure 11, curve 30). This means that the micro-VCM condensable material has a vapour pressure below that of triacontaan. The lowest vapour pressure of a contaminant at 125°C, which still gives a total mass loss of 0.1%, is 2.5×10^{-7} torr; this vapour pressure corresponds to that of heptatriacontaan $\text{C}_{37}\text{H}_{76}$.

Table 7 shows the equivalent hydrocarbons which will not pass the 0.1 CVCM limits of the micro-VCM test operating at different condenser temperatures.

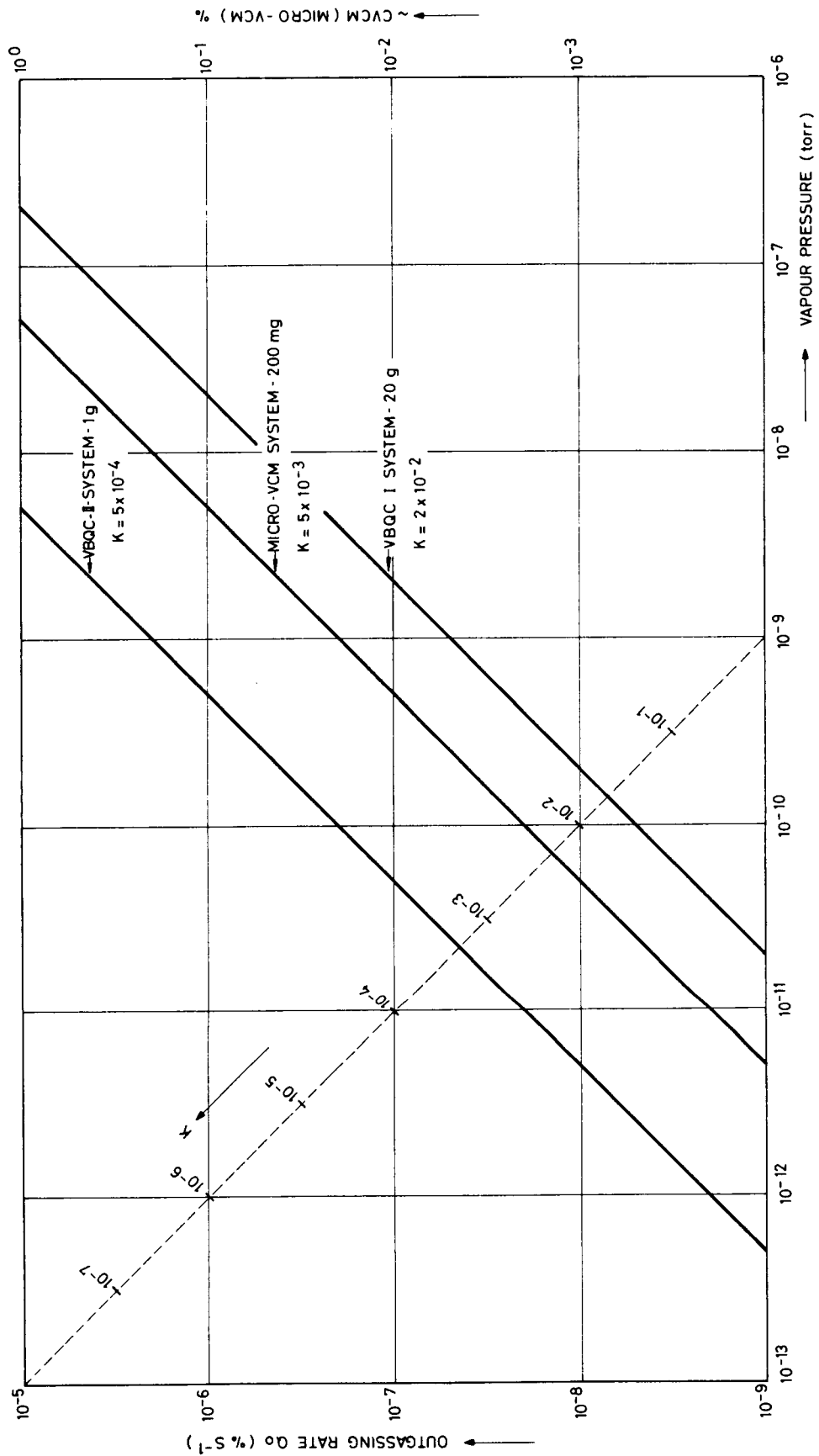


FIG.10 VAPOUR PRESSURE OF CONTAMINANTS WHICH JUST EVAPORATE AS A FUNCTION OF OUTGASSING RATE $P_S = k \cdot Q_0$

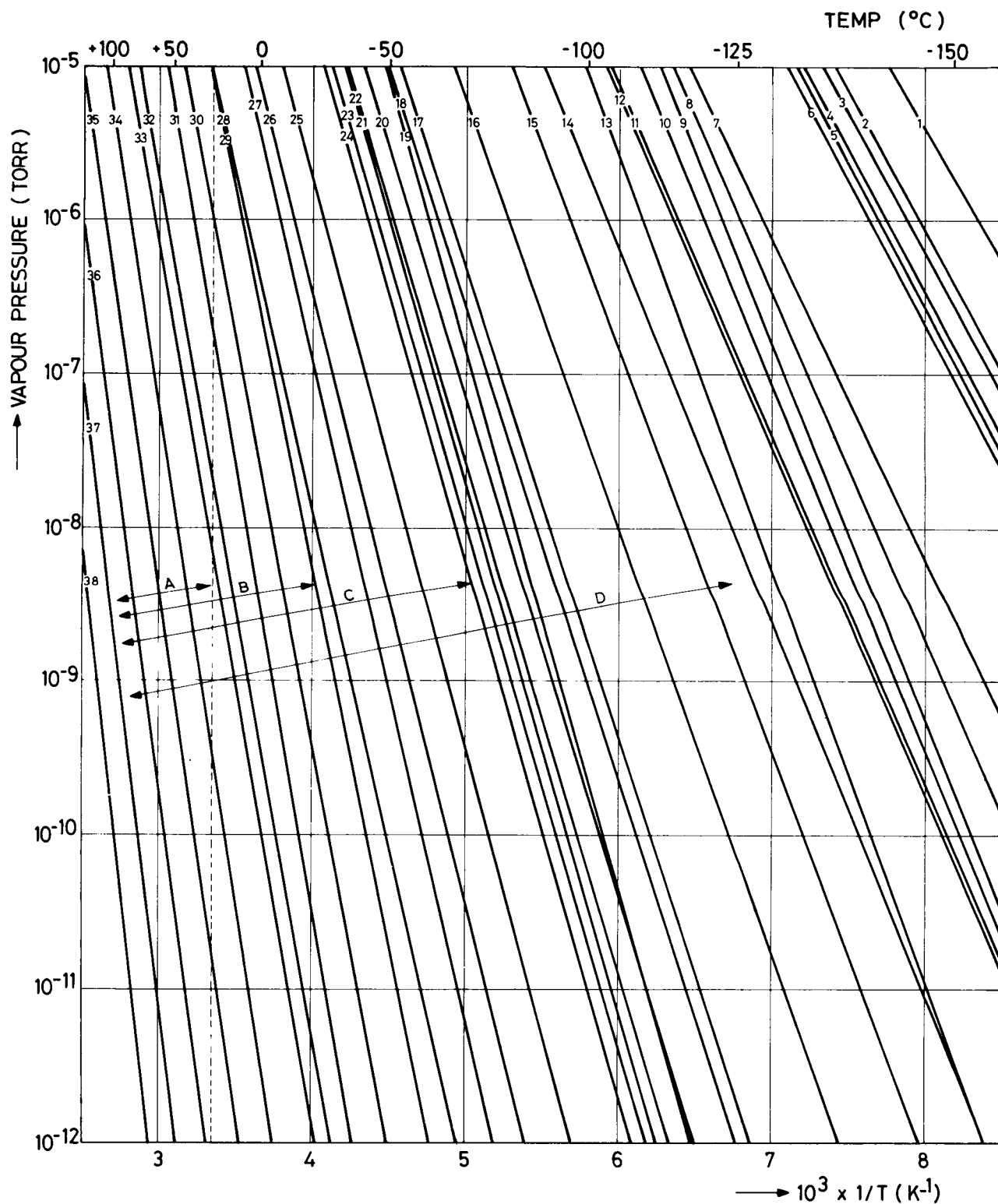


FIG.11 VAPOUR PRESSURE OF MATERIALS AS A FUNCTION OF TEMPERATURE

TABLE 7

Condenser Temp. °C	Equivalent hydrocarbons which will not pass the micro-VCM limits of 0.1% CVCM	Covering lines in Fig. 11
+ 25°C	C ₃₇ H ₇₆ - C ₃₀ H ₆₂	A
- 25°C	C ₃₇ H ₇₆ - C ₂₄ H ₅₀	B
- 75°C	C ₃₇ H ₇₆ - C ₁₆ H ₃₆	C
-125°C	C ₃₇ H ₇₆ - C ₁₀ H ₂₀	D

The flux of $1 \times 10^{-6} \% \cdot S^{-1}$, which was mentioned earlier and which will just re-evaporate in the micro-VCM system if the vapour pressure is 5×10^{-9} torr, will just evaporate in the VBQC-II system (having a "K" value of 5×10^{-4}) when the vapour pressure is 5×10^{-10} torr. This means that the materials of which the outgassing flux is $10^{-6} \%$ and the vapour pressure between 5×10^{-10} torr - 5×10^{-9} torr are measured as CVCM with the micro-VCM system and not with the VBQC-II system at the same condenser temperature.

11. CONCLUSION

A standard test method for measuring the total outgassing rate and the condensible outgassing rates of spacecraft materials can give very useful information for material selection and spacecraft contamination prediction. If the predicted levels are not acceptable, the necessary corrective actions can be taken at the early design phase. The outgassing characteristics of materials can best be studied only when the fluxes are easily measurable. In general, this means that a high configuration factor "K" is required. On the other hand, for critical spacecraft surfaces, where contamination should be as low as possible, the design to be incorporated should be such that the lowest possible "K" factor is obtained.

In practice, the prediction of spacecraft contamination requires extrapolation of the VBQC test contamination data down to realistic spacecraft contamination levels in which the "K" factor is generally much lower than the "K" factor in the VBQC test. The linear extrapolation method and the sticking coefficient method both result in "worst case" figures because the re-evaporation of condensable contaminants is not completely taken into account.

The correction method for re-evaporation of contaminants required the vapour pressure to be expressed as a function of concentration for the condensable

contaminants. These vapour pressure data may be obtained from the three methods given in this paper.

At the present time, no tests are being performed to correlate data pertaining to these three methods.

A problem in the determination of vapour pressures of condensable contaminants as a function of temperature by measuring the re-evaporation rates from the QCM's is the temperature measurement of the QCM's in our systems. Recent improvements on temperature stability of QCM's have been achieved by the use of double oscillating quartz crystals (ref. 20), even simultaneous mass and temperature determination on a QCM is possible by use of the electrode - tab configuration (ref. 21).

APPENDIX

APPENDIX: VAPOUR PRESSURES OF SOME SPACECRAFT CONTAMINANTS

The vapour pressure/temperature function of typical spacecraft contaminants such as solvents, water, methyl siloxanes, phthalate esters, phenyl-methyl siloxanes, and alkanes (hydrocarbons) is in general not known below 1 torr. Knowledge of vapour pressures down to 10^{-12} torr and the corresponding temperatures is interesting for above mentioned types of contaminants because of possible spacecraft contamination of critical surfaces.

Also interesting is the selection of materials which can be used for calibration purposes of outgassing systems and for contamination experiments.

The vapour pressures of 1, resp. 10 torr and the corresponding temperatures given in the Handbook of Chemistry and Physics (D-185) have been used for the calculation of the constants A and B in the Clapeyron equation:

$$\log P = A - \frac{B}{T}$$

In the above equation P, the vapour pressure in torr and T is the absolute temperature in K.

The A and B constants for the methyl-phenyl silicones DC705, resp. DC705 were obtained from the manufacturers data sheets.

As no better data were available, the Clapeyron equation has been used for extrapolation of the vapour pressures down to 10^{-12} torr.

The A and B constants of the 38 materials are given in attached table and the corresponding pressure/temperature functions have been plotted in attached figure.

An interesting point of the plotted vapour pressure/temperature functions is that all the lines seem to come from one point. This means that any vapour pressure of an unknown material measured at certain temperature can easily be extrapolated to a vapour pressure at another temperature.

TABLE: VAPOUR PRESSURE EQUATION ACCORDING TO CLAPEYRON

$$\log P = A - \frac{B}{T}$$

P=vapour pressure
(torr) T= temperature

NO.	CHEM.FORM.	M	NAME	A	B
1	$C_2Cl_3F_3$	188	Trichloro-trifluoro-ethane	8.408	1725
2	C_3H_6O	58	Acetone	8.555	1829
3	$CHCl_3$	120	Trichloro-methane	8.604	1852
4	C_6H_{14}	86	Hexane	8.588	1883
5	CCl_4	154	Carbontetrachloride	8.342	1862
6	C_4H_8O	72	2-Butanone (MEK)	8.349	1878
7	C_7H_8	92	Toluene	8.447	2082
8	C_2H_6O	46	Ethanol	9.341	2260
9	C_6H_6	78	Benzene	10.385	2456
10	C_3H_8O	60	2-Propanol (IPA)	9.670	2390
11	C_8H_{10}	106	3-Xylene	8.565	2281
12	$C_6H_{18}O_3Si_3$	222	Hexamethylcyclotrisiloxane	8.458	2272
13	H_2O	18	Water	10.482	2681
14	$C_{10}H_{20}$	140	Decane	8.391	2431
15	$C_8H_{24}O_4Si_4$	296	Octamethylcyclotetrasiloxane	8.906	2626
16	$C_{10}H_{30}O_5Si_5$	370	Decamethylcyclopentasiloxane	8.766	2791
17	$C_{12}H_{36}O_6Si_6$	444	Dodecamethylcyclohexasiloxane	8.974	3056
18	$C_{14}H_{42}O_7Si_7$	458	Tetradecamethylheptasiloxane	8.902	3088
19	$C_{10}H_8$	128	Naphtalene	10.812	3523
20	$C_{14}H_{42}O_7Si_7$	518	Tetradecamethylcycloheptasiloxane	8.954	3219
21	$C_{16}H_{48}O_8Si_8$	532	Hexadecamethyl octasiloxane	9.088	3330
22	$C_{15}H_{32}$	212	Pentadecane	9.328	3403
23	$C_{16}H_{48}O_8Si_8$	592	Hexadecamethylcyclo octasiloxane	9.015	3396
24	$C_{18}H_{54}O_9Si_9$	604	Octadecamethyloctasiloxane	9.148	3468
25	$C_{19}H_{40}$	269	Nonadecane	9.077	3690
26	$C_{16}H_{22}O_4$	278	Dibutyl phthalate	9.428	3973
27	$C_{20}H_{60}O_8Si_9$	680	Eicosamethylnonasiloxane	10.271	4285
28	$C_{24}H_{50}$	339	Tetracosane	9.494	4339
29	$C_{22}H_{56}O_9Si_{10}$	744	Docasamethyldecasiloxane	11.200	4855
30	$C_{24}H_{72}O_{10}Si_{11}$	828	Tetracosamethylhendecasiloxane	11.805	5293
31	$C_{16}H_{22}O_4$	278	Ethylhexyl phthalate	12.779	5814
32	?	484	DC-704-Methyl Phenyl trisiloxane	11.025	5570
33	$C_{30}H_{62}$	423	triacontane	10.977	5705
34	?	?	DC-705 Methylphenyltrisiloxane	12.118	6424
35	$C_{34}H_{70}$	479	Tetratriacontane	12.178	6861
36	$C_{36}H_{74}$	507	Hexatriacontane	12.772	7473
37	$C_{38}H_{78}$	535	Octatriacontane	13.435	8152
38	$C_{40}H_{80}$	563	Tetracontane	14.067	8841

1. J. J. SCIALDONE Prediction Spacecraft Self-Contamination in Space and in a Test Chamber. Space Simulation Conf. 1972 - NASA-SP-298.
2. D. EDLEY GEOS Outgassing Calculation and Ion Production. Study note BA-4J-324 (1975) Britsch Aircraft Corp - England.
3. W. WILKENS a.o. Experimental Study on the Contamination Degradation Effects on the Optical and Thermo-Optical Performances of Critical Parts of the METEOSAT-Radiometer in Orbit. Prepared under ESA-Contract No. 2234/74/09 by DFVLR - West Germany (1976)
4. E. A. ZEINER AESC Multinodal Free Molecular Contamination Transport Model. Space Sim. Conf. 1975 - NASA-SP-379.
5. L. E. BAREISS Preliminary Evaluation of the Contaminant Induced Environment for the Space Shuttle Orbiter. Space Simulation Conf. 1975 - NASA-SP-379.
E. B. RESS
R. O. RANTANEN
L. J. LEGER
6. R. L. HARVEY Spacecraft Neutral Self-Contamination by Molecular Outgassing. J. Spacecraft Vol 13-No. 5-May 1976.
7. L. E. BAREISS Spacelab Contamination Assessment MCR-77-105 - September 1977 - Contract MAS8-31547. Exhibit B.
M. A. HETRICK
E. B. RESS
8. D. A. WALLACE Use of the Quartz Crystal Microbalance for Outgassing and Optical Contamination Measurements. Journal of Vacuum Science and Technology 1972/Vol 9/1.
9. D. McKEOWN Thermoelectrically-Cooled Quartz Crystal Microbalance. Space Simulation Conf. 1973 - NASA-SP-336.
W. E. CORBIN
R. J. NAUMANN
10. J. T. VISENTINE Molecular Outgassing Measurements for an Element of the Shuttle Thermal Protection System. AIAA No. 76-446, 11th Thermophysics Conf., July 1976.
R. G. RICHMOND
11. R. S. PASSAMANECK Small Monopropellant Thruster Contamination Measurement in a High-Vacuum Low Temperature Facility. J. Spacecraft Vol 14 - July 1977.
J. E. CHIRIVELLA
12. R. W. PHILLIPS Spacecraft Contamination under Simulated Orbital Environment. J. Spacecraft Vol 14 - August 1977.
L. U. TOLENTINO
S. FEUERSTEIN
13. R. P. HENRY Mesure de taux de dégazage he Vide Novembre-Décembre 1969.
14. W. WILKENS Outgassing Measurements using Vacuum Balances published in "Progress in Vacuum Microbalance Techniques" Vol 2-1973.
H. BENTLAGE
15. J. J. SCIALDONE An Equivalent Energy for the Outgassing of Space Materials. NASA-TN-D-8294.
16. I. LANGMUIR The Evaporation Condensation, and Reflection of Molecules and the Mechanism of Absorption. Phys. Rev. Ser 2, Vol 8, August 1916.

17. T. M. HESLIN An Equation that Describes Material Outgassing for Contamination Modelling. NASA-TN-D-8471, May 1977.
18. J. DAUPHIN a.o.
A. ZWAAL The Outgassing of Space Materials and its Measurement. ESRO-TN-124. February 1975.
19. A. ZWAAL Contamination Analyses of OTS Radiator Panels. Internal Publication TQMAZ-7702 (1977).
20. J. Ph. TERMEULEN
F. J. Van EMPEL The Use of Double Oscillating Quartz Crystals in Mass Determination. Progress in Vacuum Microbalance Techniques Vol 1-1972.
21. E. C. Van BALLEGOOYEN
F. BOERSMA
C. v.d. STEEN Application of a Quartz Crystal with Electrode tabs Configuration for Simultaneous Mass and Temperature Determination. Journal of Acoustic Society of America, March 1978.
22. G. GOURMELON
A. ZWAAL Contamination Measurements on METEOSAT Solar Array using QCM's. ESA-EWP-1012, May 1976.